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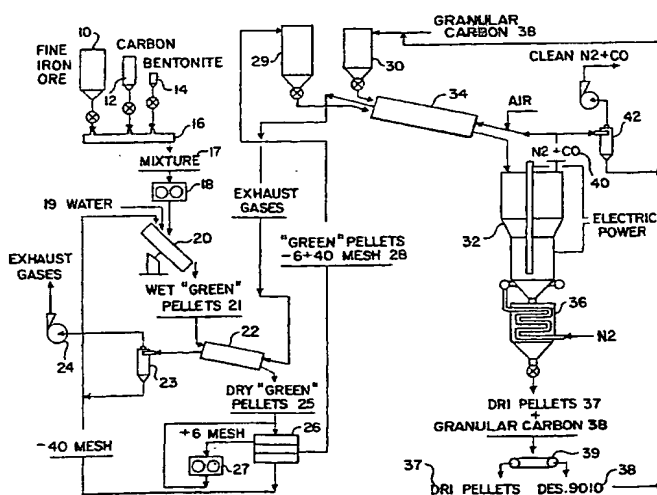
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(54) Title: PROCESS AND APPARATUS FOR THE DIRECT REDUCTION OF IRON OXIDES IN AN ELECTROTHERMAL FLUIDIZED BED AND RESULANT PRODUCT



(57) Abstract: A method and an apparatus (50) for producing direct reduced iron (37) from dry pellets (25) composed of iron oxide and carbonaceous material. A mixture of pellets (25) and free coke particles (38) with weight relation from 3:1 to 5:1 is fed into the top of an electrothermal fluidized bed (32) that is fluidized by nitrogen. By exposing pellets (25) in the electrothermal fluidized bed (32) to temperatures of between approximately 850-1,100°C for an average period of between approximately 15-60 minutes, the volatiles are removed and the pellets (25) metallized. Reduced pellets (37) mixed with free coke (38) are discharged from the bottom of fluidized bed (32) and cooled. The reduced iron pellets (37) are physically separated from any free coke (38) and the free coke (38) is recycled back into the fluidized bed (32).

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PROCESS AND APPARATUS FOR THE DIRECT REDUCTION  
OF IRON OXIDES IN AN ELECTROTHERMAL FLUIDIZED BED  
AND RESULTANT PRODUCT

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BACKGROUND

[0001] This invention relates to a process for the chemical reduction of iron oxides into metallic iron at temperatures below the melting point of iron ( $1,530^{\circ}\text{C}$ ), commonly known as "direct reduction." More specifically, the present invention is directed to a process for the direct reduction ("DR") of iron ores using solid carbon as the reductant in which the heat needed for the reduction reactions is provided by resistively heating the reactant materials while they are in a fluidized bed formed by a mixture of reactant materials and free carbonaceous particles. The invention additionally provides a unique direct reduced iron (DRI) product as a result of the inventive process.

[0002] Iron ores of various types are found in enormous amounts throughout the world. Most iron ores are oxides of iron, mainly hematite ( $\text{Fe}_2\text{O}_3$ ). To make metallic iron, the ore is chemically reduced using agents that are in most cases derived from coal or natural gas (methane). The reduction of iron oxide to form metallic iron is endothermic, that is, heat is required to achieve the removal of oxygen atoms from the iron oxide molecule.

[0003] The method most commonly used for the industrial production of iron for steelmaking is the blast furnace. The furnace itself is a tall, very large diameter, generally cylindrical steel vessel that is lined with refractories.

[0004] Lump iron ore, and now more commonly pelletized iron ore, is fed with solid carbon (coke) into the top of the blast furnace. Air is introduced near the base of the furnace to burn a portion of the carbon to generate heat and carbon monoxide. This gas then reduces the iron oxide into metallic iron. The downward movement of the ore against the

rising flow of reducing gas makes the blast furnace a highly efficient countercurrent reactor for the production of metallic iron from iron ores. The partial combustion of the coke provides the necessary heat for the reduction and for the melting of the metallic iron formed by the reduction. As the iron melts, it trickles downward through the unburned coke and forms a pool of molten metal which is periodically tapped and transferred to other vessels where it is either solidified as a high carbon "pig iron", or treated in the molten state to remove carbon and to add alloying agents to form various steel products.

[0005] Despite the excellent thermodynamic and thermal efficiency of the blast furnace for making cast iron, it has many disadvantages. Consequently, during the last 50 years the trend in new plants for production of iron from iron ores is to use direct reduction (DR) processing. Indeed, the increase in iron making capacity in recent years has been largely by DR processing.

[0006] There are a number of reasons for the rapidly increasing use of DR rather than the well established blast furnace method. For one, iron ore deposits often contain substantial amounts of very fine ore that is unsuitable for use directly in the blast furnace. A number of DR processes were originally developed to process iron ore fines without the need to first pelletize or agglomerate the ore.

[0007] Another important reason for choosing DR in place of the blast furnace is that the blast furnace requires "coking" coals. These coals, when heated to remove much of their volatile content, will form a coke material that has a reduced tendency to soften and provides the strength to support the weight of the burden of iron ore and coke that is moving downward in the furnace. Although there are numerous large coal deposits throughout the world, very few have the necessary characteristic of high strength after coking to be useful in the blast furnace. Thus, DR plants

are generally built in areas of the world where coking coals are not available and/or there is an abundant supply of natural gas.

[0008] Another reason for the popularity of DR is the flexibility of producing a granular or briquetted iron product that can be shipped elsewhere for melting and production of steel, making the full investment for an integrated steel mill unnecessary.

[0009] DR processes are of two basic types depending on whether the reducing agent is gaseous or it is a form of solid carbon. Most operating DR plants use shaft or fluidized bed (FB) furnaces using gaseous reductants derived from natural gas. These are known generally by their acronyms MIDREX, HYL, etc. Although natural gas itself is not an effective reductant, it can be converted into hydrogen or mixtures of hydrogen and carbon monoxide by "reforming". The reforming of natural gas is well established technology that involves several process reactors and catalytic conversion, thus entailing significant capital and operating costs.

[00010] Gaseous reduction systems are also generally operated at elevated pressure to increase the reduction rate and productivity per unit of reactor volume so that the vessel size can be held within the limits of practical construction. The elevated pressure requires expensive pressure vessels and the solid feed and product handling must be done using "lock hoppers." This adds significantly to the cost of the DR plant.

[00011] A basic disadvantage of DRI processes has been the heat it requires. The reduction reactions are slow at low temperature, and it is necessary to operate the reduction reactors at temperatures above 650°C to achieve reasonable processing rates. The direct partial combustion of the reducing gases within the DR reactor is a possible means to achieve the heating, but this procedure is difficult to

control and can be dangerous. Instead, the ore is preheated in a separate reactor to a temperature above the desired reduction temperature so that the excess heat provides the heat needed to maintain the desired temperature for reduction. Additionally, the reducing gas is generally preheated by indirect heat exchange before introducing it into the reduction reactor. Preheaters add complexity and cost and are not a highly efficient means to add heat to the reaction system.

[00012] For locations that do not have natural gas, DR processes have been developed that use coal as a solid reductant. The predominant processes of this type have used long, horizontal refractory lined rotary kilns as the process vessel. These processes are known generally by their acronyms SL/RN, DRC, and ACCAR/OSIL. Coal, iron ore and some limestone are fed to the kiln which is operated at temperatures between about 850-1,050°C. Auxiliary burners fired with various fuels, including pulverized coal, are generally provided to heat the charge materials from above. The rate of the reduction reactions with relatively coarse solid carbon and iron ore is not rapid, and the plants using this type of reducing reactor are limited in capacity to approximately 100,000 metric tons per year. The rotary kiln processes are subject to the problem of the tendency for the formation of accretions on the wall of the kiln. Although rotary kiln based DR plants have been built in many places of the world, the combined annual capacity of these is less than 2.5 million metric tons, which constitutes less than 5 percent of the total DR production capacity.

[00013] Another type of coal or solid carbon reductant process developed during the past 20 years employs a rotary hearth rather than a rotary kiln. These processes are known generally by their acronyms Inmetco and FASTMET. To improve the reaction kinetics and to avoid the tendency for agglomeration to occur within the reducing reactor, the

rotary hearth processes have used a feed of pelletized iron ore fines which also contain the carbon reductant within the pellets. Various types of fine coal are generally used as the reductant. The intimate contact between the fine particles of iron ore and the fine carbon, in combination with a significantly higher operational temperature (1,205-1,450°C), provides a relatively rapid rate of reduction compared with the rotary kiln processes. The heating is also done through use of auxiliary burners positioned in the roof of the rotary hearth furnace. These can be operated with various fuels. Heat may also be generated by burning a portion of the combustible gases (primarily CO) produced by the reduction reactions and any volatile matter that evolves from the coal. The source of heat within the rotary hearth furnace, as in the rotary kiln, is generated above the charge material, and the rate of heating is largely by radiation from the flames above. To achieve reasonable rates of heat transfer to the charge to sustain the reduction, it is necessary to limit the thickness of the layers of pellets on the hearth to only two or three times the maximal pellet diameter (20-40 mm). Higher temperatures (1,250-1,450°C) are used than in the rotary kiln processes and, with the use of pellets containing the reductant, the reduction rate is higher. However, the throughput is limited by the restriction of having only very thin layers of the reacting pellets on the hearth.

[00014] It is worth noting that while most of the world capacity for directly reduced iron (DRI) is based on processes that employ gaseous reductants in moving-beds (shaft kilns), such as the MIDREX and HYL processes, the more recently built DR plants have selected fluidized-bed processes, known by their acronyms FIOR/FINMET and CIRCORED. As discussed above, the fluidized-bed processes offer the advantage of processing iron ore fines without requiring pelletization. They also offer very efficient contact

between the particles of iron ore and the gaseous reductant. In addition, they provide extremely high heat transfer rates and excellent temperature control. However, the fluidized-bed processes of the prior art have all used gaseous reductants and have the same limitations as shaft processes as relates to the heat requirements and temperature limitations. No prior art DR process has used fluidized-bed technology for the direct reduction of iron ore with solid reductants.

[00015] Accordingly, it is the primary object of the present invention to provide a process for the direct reduction of iron oxides in a fluidized-bed reaction vessel using solid carbon as the reducing agent.

[00016] It is also an object of the present invention to provide a process for the reduction of iron oxides in a fluidized-bed at significantly higher temperatures, and therefore higher reduction rates (and, thus, production rates), than that achieved in the present processes for the fluidized-bed gaseous reduction of iron oxides.

[00017] It is a further object of this invention to provide the heat needed to sustain the reduction reaction and maintain the desired reaction temperature by use of highly thermally efficient electrothermal or charge-resistance heating.

[00018] It is still another object of this invention to increase the production rates to rates that are significantly higher than those reported for the prior art DR processes that employ solid reductants.

#### SUMMARY OF THE INVENTION

[00019] These objects, as well as others that will become apparent upon reference to the following detailed description and accompanying drawings are provided by a direct reduction process that uses an electrothermal fluidized-bed (EFB) furnace containing a fluidized-bed of electrically conductive granular carbon (coke, char, etc.)



which serves as a heating element for the electrothermal conversion of electrical energy into heat. "Self-reducing" pellets (green pellets for producing DRI) are prepared and comprise fine iron oxide (ore) in intimate association with fine carbon, which serves as the agent for reduction of the iron oxide. Introducing these pellets into the EFB furnace causes the pellets to be heated to a temperature of 850-1,100°C, which is not only sufficient for a high rate of reduction reaction to occur, but also to cause the reduced pellets to shrink in size due to sintering of the metallic iron formed by the reduction of the oxide. The shrinkage results in a lower internal porosity of the pellets and a correspondingly higher pellet density. This creates a migration of the reduced pellets downward through the upper fluidized bed which contains relatively low density granular carbon, green pellets and partially reduced pellets that serve as the heating element. Electrical power is used to cause electrical current flow through the fluidized bed to generate heat through the  $I^2R$  conversion. The application of electrical power is controlled to maintain the temperature within the EFB at a level that causes the reduction reaction with simultaneous partial sintering within the pellets.

[00020] Another aspect of the invention, the fluidized bed portion of the furnace, is designed so as to include two distinct zones, namely, an upper zone with vertical walls and a generally constant cross-sectional area and a lower zone of a reduced cross-sectional area that terminates in an inverted conical section in which the fluidizing gas distributor is located. This design provides for active fluidization in the top zone of a particulate mixture having a high concentration of granular carbon and green DRI pellets and a low concentration of reduced DRI pellets. A mixture of reduced DRI pellets with a low content of granular carbon is fluidized in the lower zone. To prevent particle agglomeration and deposition formation on the

interior of the furnace, the furnace is designed without any interior horizontal surfaces. More particularly, all internal surfaces are at an angle equal to or greater than the angle of repose for the reduced pellets. The electrodes that enter the fluidized bed to enable current flow therethrough are positioned to be in contact only with the upper fluidized bed zone that is rich in granular carbon. This minimizes the possibility of heating the iron-rich pellets to a temperature above the melting point of metallic iron, which would cause uncontrolled agglomeration of iron onto the surface of the electrodes and other internal surfaces.

[00021] Other objects and advantages of the process of this invention will become evident from the following description of the process, equipment and methods of operation.

#### BRIEF DESCRIPTION OF THE DRAWINGS

[00022] The foregoing and other objects will be more readily apparent by referring to the following detailed description and the appended drawings in which:

[00023] Fig. 1 is a vertical cross-sectional view of an electrothermal fluidized bed furnace according to one aspect of the present invention.

[00024] Fig. 2 is a schematic diagram of the process for a method of achieving rapid and efficient reduction of iron oxide in an electrothermal fluidized bed furnace according to another aspect of the present invention.

#### DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[00025] In keeping with the invention, the reduction of the iron ore pellets is conducted in a fluidized bed comprising a mixture of coarse carbon particles (coke such as petroleum or metallurgical coke, coal with low sulfur content, pure synthetic graphite, etc.) and partially-reduced iron ore pellets. Carbon particles provide electrical conductivity for the fluidized bed and heat

generation internally within the fluidized bed is due to passing the electrical current through fluidized bed. Further, the carbon-rich fluidized bed zone helps to reduce the product gases back from  $\text{CO}_2$  to CO and, if water is present, to CO and  $\text{H}_2$ . The dimensions of the dry green pellets and carbon particles are chosen to provide uniform fluidization of both materials with a degree of reduction of less than 25-35 percent. The apparent specific density of DRI pellets changes from 2.1-2.25 g/cc, for pellets with  $\text{Fe}_2\text{O}_3$  content of approximately 75 percent (and approximately 50 percent of total iron), to 4.2-5.2 g/cc for reduced pellets with total iron content of approximately 80-85 percent and  $\text{Fe}_2\text{O}_3$  of approximately 2-5 percent. The shrinkage in volume of DRI pellets is between approximately 25-35 percent. While the inventive process has particular utility for the direct reduction of iron oxide, other metallic oxides, such as nickel oxide ( $\text{NiO}$ ), vanadium oxide ( $\text{V}_2\text{O}_5$ ), tungsten oxide ( $\text{WO}$ ), and oxides of cobalt (Co) and chromium (Cr), etc., may also be reduced by the inventive process.

[00026] It has been found that essentially complete reduction of the iron ore contained within the pellets occurs with less than the stoichiometric consumption of the carbon contained within the pellets. This suggests that some of the free carbon in the fluidized bed serves as a reductant as well as providing electrical conductivity. Thus, the amount of carbon added to the green pellets conceivably could be reduced or possibly eliminated. This also suggests that the pelletizing steps may be eliminated, and that iron ore that is crushed and sized could be directly introduced into the electrothermal fluidized bed ("EFB") furnace after preheating. The amount of carbon in the reduced pellets can also be adjusted to suit the needs of the subsequent steel production. (See Example 3, *infra*.)

[00027] Turning to Fig. 1, a mixture of green iron ore

pellets containing carbon as the reductant and having a bulk density of about 2.1-2.5 g/cc is mixed with granular carbon having a bulk density of 0.75-1.1 g/cc. These do not necessarily have to be pre-mixed before feeding to furnace. These materials could be fed separately through the same or another feed port. The EFB furnace, generally designated 50, comprises a housing vessel having an upper fluidized bed section 52a with vertical walls and a generally constant cross-sectional area and a lower fluidized bed portion 52b that has a reduced cross-sectional area as compared to the upper section 52a. Preferably the cross-sectional area of the upper section 52a is from 2 to 5 times greater than the cross-sectional area of section 52b. Stated alternatively, for circular cross-sections, the diameter of section 52a is from 1.5 to 2.5 times greater than the diameter of section 52b. As illustrated, the lower fluidized bed portion 52b is conical in cross-section. However, other shapes may also be utilized so long as the reduced cross-sectional area with respect to section 52a is maintained. For example, section 52b may also have vertical walls throughout its major portion and terminate in a conical section, with a tapered transition joining sections 52a and 52b.

[00028] A lower fluidizing gas distribution section 54 depends from section 52b which has sloping walls and a cross-sectional area that decreases from its upper end toward its bottom. These furnace sections are preferably cylindrical, with a circular horizontal cross-section, or oval, with an ellipsoidal horizontal cross-section. Also, several such furnaces may be ganged together to form an array, thus providing for increased capacity.

[00029] The pellets and granular carbon are fed into the EFB furnace 50 through inlet 60 and falls through furnace freeboard space 62 and into the upper part of the fluidized-bed of material contained in section 52a. Fluidizing gas is made to enter the base of EFB furnace 50 into conical

section 54 through nozzles 66. As the pellets become reduced, the density of the pellets increases to a density higher than that which can be fluidized by the rising gases within section 52a. These denser pellets move downward into the lower, smaller diameter fluidized bed section 52b and into conical or tapered section 54 where the gas velocity is higher and thus capable of fluidizing the denser partially reduced pellets.

[00030] Because the coke particles are substantially less dense than either the green pellets or the partially reduced pellets, the majority of the coke particles remain in the upper section 52a, whereas the denser, partially reduced pellets are contained mainly in lower section 52b. However, because of the substantial turbulence created by the high velocity of the gas entering section 54, there is considerable mixing of the material contained within the two zones of fluidization. When the iron ore pellets are fully reduced, the density becomes 4.2-5.2 g/cc, and at this higher density they move to the lower part of conical section 54 and are removed through discharge feeder 64.

[00031] As seen in profile, the lower portion 54 has a conical appearance. Importantly, the slope of the walls in the lower section must be steeper than the angle of repose for the reduced pellets (preferably 15-20° from vertical) so that none collect on the walls of the lower section. The reduced cross-sectional area of the lower section 54 promotes the separation and segregation of the free coke from the pellets and the re-circulation of the pellets into the upper section 52a of the furnace 50.

[00032] Optionally, in the illustrated embodiment the fluidizing gas is fed to the nozzles through a tubular heat exchanger 68 that encircles the lower section 54 before connecting to a manifold that includes the inlet nozzles 66. In this way, the temperature of the fluidizing gas is raised before it is injected into the furnace, while the

temperature of the reduced pellets that pass through the lower section 54 is lowered to a temperature more likely to inhibit the reoxidation and agglomeration of the reduced pellets. Optionally, a separate heat exchanger may be provided below the bottom of section 54 for which the fluidizing gas may also be used as the coolant. The spent fluidizing gas and the gaseous products of reduction (CO) exit the freeboard space 62 through a flue outlet 70. The gas can be advantageously used to dry and pre-heat the green pellets and/or as a fuel in related steel making steps in an integrated steel-making facility to, e.g., melt the reduced pellets, resulting in potential cost savings from reducing the need for other energy sources.

[00033] The electrothermal heating of the furnace is accomplished by locating one or more vertically-oriented electrodes 56 of a first polarity spaced from the walls of upper fluidized bed section 52a. There can be a number of ways to locate electrodes. For example, with a cylindrical process vessel and using 3-phase AC electrical power, three electrodes could be located spaced away from the inner walls. If one or more electrodes 58 of opposite polarity are located along the inner walls of upper section 52a, a voltage applied across the electrodes 56 and 58 would cause electric current to flow from electrode(s) 58 through the fluidized-bed of material contained in section 52a. The electrodes 56, 58 may be graphite, baked carbon, etc. The presence of substantial carbon in section 52a provides sufficient electrical conductivity to allow current to flow through the bed of fluidized solids contained in section 52a and generate the heat needed for the reduction by direct resistive heating of the material in section 52a. Although the resistive heating occurs essentially entirely within section 52a, the high degree of mixing of the materials in section 52a and section 52b provides effective heating of the denser iron ore particles throughout the time of their

residence within the EFB furnace such that the reduction reactions continue to completion.

[00034] The residence time of the pellets within the reaction zone (or fluidized bed) is dependent on the amount of material contained within the fluidized bed and the rate of feeding of the pellets to the furnace. It follows therefore that for a furnace of a given cross-section, the residence time can be varied by varying the feed rate and by independently varying the height of the fluidized bed in section 52 to accommodate a greater amount of material. This feature illustrates one of the major differences in the fluidized-bed furnace from the rotary hearth type that has limited ability to increase residence time except by reducing the throughput.

[00035] Referring now to the flow sheet of the inventive method and apparatus for reduction of iron oxide in an EFB furnace shown in Fig. 2, the iron ore is first pelletized in the well-known manner. To this end, the process includes three feed bins, 10, 12 and 14, that contain the raw materials for the process. Feed bin 10 contains iron oxide (iron ore fines, iron oxide concentrates, etc.); feed bin 12 contains solid reductant (green petroleum coke, pulverized coal, coke breeze, petroleum coke, light coal, etc.); and feed bin 14 contains binder (bentonite, organic resin, etc.). The iron oxide and solid reductant are preferably in the form of particles sized smaller than 100 mesh, and more preferably smaller than 150 mesh, to insure good contact therebetween. Further, the solid reductant preferably has a low sulfur content (from between 0.3 to 1.0 percent (wt.)), a low ash content (less than 2 percent (wt.)), and a volatile content ( $C_nH_m$ ) of greater than 2 percent (wt.). In the pellets, the carbon reductant is present in an amount preferably from 22.5 percent (wt.) to 28 percent (wt.) of the iron oxide, with the amount of carbon in the pellets being from 1.0 to 1.25 times the amount theoretically

required for the reduction reaction of  $\text{Fe}_2\text{O}_3 + 3\text{C} = 2\text{Fe} + 3\text{CO}$ . The ratio may change depending upon the type of metal oxide and the reaction conditions.

[00036] Raw materials from the feed bins 10, 12 and 14 are mixed together in proper proportions in a blender 16. Preferably, the dry mixture contains approximately 75 percent (by weight) iron oxide, up to approximately 23 percent (by weight) solid reductant, and approximately 1 to 2 percent (by weight) binder. The mixture 17 is then processed through a size reduction mill 18 to reduce the components to a generally uniformly-sized powder. The powdered materials are then introduced to a pelletizer 20, where water is also added, to form "wet" green pellets 21.

[00037] The green pellets 21 are transported to a dryer 22 where they are dried at between approximately 110-130°C (230-260°F) to remove moisture to less than 0.5-1.0 percent. The exhaust gases from the dryer 22 are passed through a cyclone 23. Any dust in the gas is recycled back to the blender 16 or to the pelletizer 20 for reprocessing into green pellets. The exhaust gas is then pumped by exhauster 24 through an electrostatic precipitator or other type dust collector before being exhausted to atmosphere.

[00038] The dry green pellets 25 are then sent to screener 26 to separate out pellets that are sized between 6 mesh and 40 mesh (-3.5 + 0.425 mm). The pellets larger than 6 mesh are sent to a size reduction mill 27 to be reduced in size, and then returned to the screener 26 to be redivided. Pellets smaller than 40 mesh are recycled directly to the pelletizer 20 to be reformed.

[00039] The dry green pellets with sizes between 6 and 40 mesh are loaded into the bin 29, and from it into an EFB furnace 32. As illustrated, the dry pellets are passed through a heater 34 before entry into the EFB furnace 32. The fresh coke (coal, coke or other material having good electrical conductivity) can be used. This fresh coke can



be supplemented with coke recovered as the non-magnetic fraction by magnet separation of the mixture of coke and reduced pellets, is loaded into the EFB furnace from the bin 30 in proper proportion with the dry green iron oxide pellets, preferably in a ratio of between about 3:1 and 5:1 (by weight) of iron oxide pellets to free coke. Any low cost, high content granular carbon material with low sulfur content may be used. Preferably, the granular carbon has a particle size smaller than 3.36 mm (-4 mesh) and larger than 0.3 mm (+50 mesh). However, the size range may vary depending upon the green pellet sizes and the velocity of the fluidizing gas.

[00040] The solid particles are fluidized by a gas, which may be nitrogen or carbon monoxide, recirculated furnace gases (such as CO), hydrogen (H<sub>2</sub>), and natural gas (CH<sub>4</sub>). Importantly, the presence of gaseous reductant in the fluidizing gas increases the rate of DRI pellet reduction and affects the residue content of free carbon in the reduced DRI pellets so that it falls within a range of from 1 to 20 wt. percent. Thus, the initial carbon content of the green DRI pellets can be reduced to below the stoichiometric amount due to the gaseous reductant in the fluidizing gas. The gaseous reductant results from the Boudouard reaction ( $C + CO_2 = 2CO$ ) that occurs concurrently with the iron oxide reduction ( $Fe_2O_3 + 1.5C = 2Fe + 1.5 CO_2$ ), and proceeds at a high rate due to the temperature of 850-1,100°C and the presence of excess free carbon in the fluidized bed.

[00041] The fluidizing gas is introduced into the bottom of the conical section of EFB furnace 32. The green pellets are reduced in the fluidized bed at temperatures between approximately 850-1,100°C (1,562-2,012°F) and residence times of between approximately 15-60 minutes. The reduced DRI pellets 37 and minor amounts of carbon particles 38 are discharged from EFB furnace 32, cooled in a heat exchanger

36, and sent to a magnetic separator 39. The reduced pellets are preferably cooled to prevent iron reoxidation and particle agglomeration. The reduced DRI pellets with a total iron content of 85-95 percent and a carbon content of 5-15 percent are separated from the free coke by common physical separation methods, such as magnetic separation.

[00042] After separation from the reduced pellets, the free carbon is returned to the bin 30 and loaded back into the EFB furnace 32 for fluidized bed stabilization. The flue gas 40 from the EFB furnace may be cleaned in a cyclone 42. The collected dust is sent back to the bin 30. If a large amount of iron ore is in the dust, the dust can be stockpiled and the fine particles of iron ore separated out. The flue gas from the cyclone 42 is cleaned by a bag house or electrostatic precipitator 44 and may be either burned and exhausted to the atmosphere or recycled. As shown, part of the clean mixture of nitrogen and carbon monoxide 43 is recycled and burned for pellet drying in the dryer 22, while part of the EFB furnace flue gas 40 can be used directly, without cleaning, for preheating of the pelletized iron ore in the heater 34 before introduction into the EFB furnace 32. The hot exhaust from the heater 34 can also be recycled to the pellet dryer 22.

[00043] As discussed above, an EFB furnace is provided that is particularly suited for use in the direct reduction of iron oxide set forth above. The fluidized bed of an EFB furnace for DRI pellet production is designed to have a fluidized bed zone with a top zone having vertical walls and constant cross-sectional area and bottom zone having a reduced cross-sectional area, with a smooth transition from the top zone of fluidized bed to the bottom zone of the fluidized bed. This provides a decreasing gas velocity from the bottom of the fluidized bed to the top of the fluidized bed. Due to the differences in density of granular carbon particles and reduced pellets, the granular carbon

circulates within the entire fluidized bed. DRI pellets with a low degree of reduction circulate in the top zone of the fluidized bed, while the iron-rich pellets concentrate in the bottom zone of the fluidized bed. Consequently, active mixing of particles occurs within both fluidized bed zones and rapid heat transfer between the zones is promoted.

EXAMPLE 1: DRI

[00044] The production of DRI pellets was conducted at the following operation parameters in a pilot EFB furnace having an inside FB diameter of 61 cm (24 in.). (In this example, as well as Examples 2 and 3, infra., Flexi coke brand of petroleum coke and Desulco 9010 brand of granular carbon were used for expediency.)

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"Green" DRI pellets

## Composition:

Fine iron oxide (99.3% Fe<sub>2</sub>O<sub>3</sub>, 100% < 100 mesh, <150 μm) - 75%  
 Flexi coke (~6% of volatile components, 100% <100 mesh) - 23.5%  
 Bentonite (100% < 100 mesh) - 1.5%  
 Pellet size: - 8 +40 mesh  
 - 2.35 + 0.425 mm  
 Specific density : 2.2-2.5 g/cc

Feeding:

Mixture of "Green" DRI pellets and heat treated coke  
 "Desulco 9010"

Composition: "Green" DRI pellets : Desulco 9010 70 : 30  
 "Desulco 9010" particle sizes: - 4 + 30 mesh  
 4.75 + 0.6 mm

Process parameters

Feeding rate: 105 -115 lb/hr  
 Average power applied 120 - 125 kW  
 Nitrogen rate: 38 - 45 scf/min  
 Inlet N<sub>2</sub> pressure 30 - 45 in. H<sub>2</sub>O  
 Operation FB temperature: 1020 -1050°C  
 Average retention time of DRI pellets in FB: ~ 1 hr  
 Discharge rate of mixture "DRI" pellets and  
 Desulco 9010: 66 - 70 lb/hr  
 Discharge composition:  
 Magnetic fraction (reduced DRI pellets): 70 - 72%  
 Desulco 9010: 28 - 30%

Magnetic fraction composition:

Total Iron (Fe tot): 83 - 88 %,w  
 Fe metallic: 76 - 83 %,w  
 C -all carbon chemically free 12 - 17%,w,  
 Degree of iron reduction: 92 -94%  
 Density of reduced DRI pellets: 4.75 - 5.2 g/cc

[00045] The DRI pellets resulting from this method exhibited a very low rate of reoxidation. Specifically, the content of metallic Fe in the pellets was substantially unchanged when measured six months after reduction. This is believed to result from some of the carbon acting as a protection against oxidation, as well as the slow cooling of the reduced pellets in a non-reactive N<sub>2</sub> atmosphere.

EXAMPLE 2: DIRECT REDUCTION OF IRON OXIDE FINES IN  
ELECTROTHERMAL FB WITHOUT PRELIMINARY  
PREPARATION

[00046] The direct reduction of iron oxide fines without any preliminary preparation (i.e., pelletizing) was conducted at the following operation parameters in a pilot EFB furnace with inside FB diameter of 61 cm (24 in.).

Fine iron oxide:	99.3% Fe <sub>2</sub> O <sub>3</sub> , 100% < 100 mesh, <150 µm
Flexi coke:	volatile components -2.7% free carbon - 94% sulfur-0.9% 0.9% 100% <100 mesh
"Desulco 9010" particle sizes:	- 4 + 30 mesh 4.75 + 0.6 mm

Feeding:

Mixture of Iron oxide fines + Flexi coke + "Desulco 9010"

Composition: Iron oxide fines	50%,w
Flexi coke	15%,w
"Desulco 9010"	35%,w

Process parameters:

Feeding rate:	85 - 90 lb/hr
Average applied power:	95 - 105 kW
Nitrogen rate:	18 - 25 scf/min
Inlet N <sub>2</sub> pressure:	20 - 35 in. H <sub>2</sub> O
Operation FB temperature:	920 - 960°C
Average retention time of DRI pellets in FB:	~ 1 hr
Discharge rate of mixture "DRI" pellets and Desulco 9010:	48 - 50 lb/hr

Discharge composition:

Magnetic fraction (reduced DRI pellets):	40 - 42%
Desulco 9010:	58 - 60 %

Magnetic fraction composition:

Total Iron (Fe tot):	95 - 96 %,w
Fe metallic:	91 - 93 %,w
C -all carbon chemically free.	1.4 - 1.5%,w,
Degree of iron reduction:	96 -97.6%

EXAMPLE 3: PRODUCTION OF IRON-BEARING CARBON PELLETS

[00047] In this example, production of iron-bearing carbon (IBC) pellets was conducted at the following operational parameters in a pilot EFB furnace with an inside FB diameter of 61 cm (24 in.).

## IBC pellets

Composition:

Fine iron oxide (99.3% Fe <sub>2</sub> O <sub>3</sub> , 100% <100 mesh, <150 μm):	50 - 60%
Flexi coke (~6% of volatile components, 100% <100 mesh):	-38 - 48%
Bentonite (100% < 100 mesh)	-2%
Pellet size:	-8 +40 mesh
	- 2.35 + 0.425 mm
Specific bulk density:	1.05-1.55 g/cc

Feeding:

Mixture of "Green" IBC pellets and heat treated coke Desulco 9010"

Composition:

"Green" IBC pellets (50/48): Desulco 9010	75:25
"Green" IBC pellets (60/38): Desulco 9010	70:30

"Desulco 9010" particle sizes:

- 4 + 30 mesh
4.75 + 0.6 mm

Process parameters:

Feeding rate:	120 -130 lb/hr
Average applied power:	78 - 85 kW
Nitrogen rate:	
"Green" IBC pellets (50/48): Desulco 9010	20-21 scf/min
"Green" IBC pellets (60/38): Desulco 9010	24-25 scf/min
Inlet N <sub>2</sub> pressure:	20 - 30 in. H <sub>2</sub> O
Operation FB temperature:	915 - 950°C
Average retention time of DRI pellets in FB:	~ 45 min
Discharge rate of mixture	
IBC pellets (50/48) and Desulco 9010:	92 - 100 lb/hr
IBC pellets (60/38): Desulco 9010	105 - 113 lb/hr
Content of magnetic fraction in the discharge	
IBC pellets (50/48):	~ 59%
IBC pellets (60/38):	~ 66%

Magnetic fraction composition:

IBC pellets (50/48):	
Total Iron (Fe tot):	55 - 59%,w
Fe metallic:	49 - 54%,w
C -(all carbon is chemically free)	41 - 45%,w,
Degree of iron reduction:	89 - 92%
IBC pellets (60/38):	
Total Iron (Fe tot):	59 - 60%,w
Fe metal:	57 - 58.5%,w
C -(all carbon is chemically free)	40 - 41%,w,
Degree of iron reduction:	96 -98%

[00048] Accordingly, a DR process meeting all the objects of the present invention has been provided. The EFB furnace provides for a controlled thermal reaction and the reduced cross-section of the fluidizing gas distribution portion of the furnace promotes segregation of the free carbon from the reduced pellets. Test results with this process show that properly formed dry pellets mixed with free coke with a weight relation from approximately 3:1 to approximately 5:1 can be reduced in EFB furnace with the fluidized bed formed initially by the same type of coke at temperatures between approximately 850-1,100°C with direct furnace heating by electrical power without agglomeration of reduced pellets. The reduction of relatively small sized iron oxide pellets and the relatively high thermal conductivity and rate of diffusion leads to increased production by a factor of 2-4 times at temperatures 250-400°C less than processes using solid carbon reductants. The use of electrical power for direct heating provides for a simple furnace design. The effluent gases, mainly CO, can be used as a fuel for drying and pre-heating the iron oxide pellets and for melting the DRI product to achieve improved overall thermal efficiency.

## WHAT IS CLAIMED:

1. A method for the chemical reduction of metallic oxides comprising:

forming pellets of metallic oxide and particulate carbon;  
providing an electrothermal fluidized bed furnace and establishing a fluidized bed of granular carbon therein;

heating the fluidized bed of granular carbon by passing electrical current through said fluidized bed;

introducing the pellets of metallic oxide and particulate carbon into the heated fluidized bed of granular carbon;

providing a fluidizing gas through the furnace at a flow rate sufficient to maintain the granular carbon and metallic oxide/particulate carbon pellets in the fluidized bed;

maintaining the fluidized bed at a temperature sufficient to cause a chemical reduction reaction of the metallic oxide and particulate carbon within the pellets;

removing the chemically reduced pellets from the furnace;  
and

exhausting effluent gases comprising fluidizing gas and gases resulting from the reduction reaction from the furnace.

2. The method of Claim 1 wherein the metallic oxide comprises metallic oxides that can be carbothermically reduced to a metallic phase in the presence of carbon below the melting point of the metal constituent of the metallic oxide.

3. The method of Claim 2 wherein the metallic oxides are selected from the group comprising iron ore, iron oxide, vanadium oxide, nickel oxide, tungsten oxide, cobalt oxide, and chromium oxide.

4. The method of Claim 1 wherein the fluidized bed is maintained at a temperature from 850°C to 1,100°C.

5. The method of Claim 1 wherein the metallic oxide/particulate carbon pellets are maintained in the fluidized bed for from 15 minutes to 60 minutes.



6. The method of Claim 1 further comprising separating the reduced pellets from any granular carbon removed from the furnace therewith.

7. The method of Claim 6 further comprising recycling the separated granular carbon by reintroducing it into the fluidized bed.

8. The method of Claim 1 wherein the fluidizing gas is selected from the group comprising nitrogen, carbon monoxide, hydrogen and natural gas.

9. The method of Claim 1 wherein the effluent gases are recycled to serve as the fluidizing gas.

10. The method of Claim 1 wherein the granular carbon of the fluidized bed is selected from the group comprising metallurgical coke, petroleum coke, coal and graphite.

11. The method of Claim 1 wherein the granular carbon is sized from 0.3 mm (+50 mesh) to 3.36 mm (-4 mesh).

12. The method of Claim 1 wherein the metallic oxide and particulate carbon both have a particle size of less than 150  $\mu\text{m}$  (-100 mesh).

13. The method of Claim 1 wherein the metallic oxide and particulate carbon both have particle sizes of less than 100  $\mu\text{m}$  (-150 mesh).

14. The method of Claim 1 wherein the particulate carbon in the pellets is from 22.5 wt.% to 28 wt.% of the metallic oxide.

15. The method of Claim 1 wherein the pellets are sized from 0.425 mm (+40 mesh) to 3.5 mm (-6 mesh).

16. The method of Claim 1 wherein the pressure within the fluidized bed is approximately equal to atmospheric pressure.

17. A free-flowing directly reduced granular iron pellet containing metallic iron dispersed within a matrix of partially reduced iron oxides and free carbon having a particle density within the range of 4.2 g/cc and 5.2 g/cc.

18. A method for the chemical reduction of metallic oxides comprising:

providing an electrothermal fluidized bed furnace and establishing a fluidized bed of granular carbon therein;

heating the fluidized bed of granular carbon by passing electrical current through said fluidized bed;

introducing fine particles of metallic oxide into the heated fluidized bed of granular carbon;

providing a fluidizing gas through the furnace at a flow rate sufficient to maintain the granular carbon and metallic oxide in the fluidized bed;

maintaining the fluidized bed at a temperature sufficient to cause a chemical reduction reaction of the metallic oxide and particulate carbon;

removing the chemically reduced metallic oxide from the furnace; and

exhausting effluent gases comprising fluidizing gas and gases resulting from the reduction reaction from the furnace.

19. The method of Claim 18 wherein the metallic oxide comprises metallic oxides that can be carbothermically reduced to a metallic phase in the presence of carbon below the melting point of the metal constituent of the metallic oxide.

20. The method of Claim 19 wherein the metallic oxides are selected from the group comprising iron ore, iron oxide, vanadium oxide, nickel oxide, tungsten oxide, cobalt oxide, and chromium oxide.

21. The method of Claim 18 wherein the fluidized bed is maintained at a temperature from 850°C to 1,100°C.

22. The method of Claim 18 wherein the metallic oxide is maintained in the fluidized bed for from 15 minutes to 60 minutes.

23. The method of Claim 18 further comprising separating the reduced metallic oxide from any granular carbon removed from the furnace therewith.

24. The method of Claim 23 further comprising recycling the separated granular carbon by reintroducing it into the fluidized bed.

25. The method of Claim 18 wherein the fluidizing gas is selected from the group comprising nitrogen, carbon monoxide, hydrogen and natural gas.
26. The method of Claim 18 wherein the effluent gases are recycled to serve as the fluidizing gas.
27. The method of Claim 18 wherein the granular carbon of the fluidized bed is selected from the group comprising metallurgical coke, petroleum coke, coal and graphite.
28. The method of Claim 18 wherein the granular carbon is sized from 0.3 mm (+50 mesh) to 3.36 mm (-4 mesh).
29. The method of Claim 18 wherein the metallic oxide has a particle size of less than 150  $\mu$ m (-100 mesh).
30. The method of Claim 18 wherein the metallic oxide has a particle size of less than 100  $\mu$ m (-150 mesh).
31. The method of Claim 18 wherein the pressure within the fluidized bed is approximately equal to atmospheric pressure.
32. The method of Claim 18 further comprising forming pellets of the fine particles of metallic oxide with particulate carbon prior to introduction into the heated fluidized bed.
33. The method of Claim 32 wherein the particulate carbon in the pellets is from 22.5 wt.% to 28 wt.% of the metallic oxide.
34. The method of Claim 32 wherein the pellets are sized from 0.425 mm (+40 mesh) to 3.5 mm (-6 mesh).
35. An electrothermal fluidized bed furnace comprising:
  - a furnace body defining a fluidized bed zone, an overbed zone disposed above the fluidized bed zone, and a discharge zone disposed below the fluidized bed zone, the fluidized bed zone comprising a first portion and a second portion disposed above the first portion and having a cross-sectional area larger than that of the first portion, the first portion defining a lower fluidizing zone and the second portion defining an upper fluidizing zone;
  - at least one electrode disposed generally centrally within the furnace body and extending into the upper fluidizing zone but not into the lower fluidizing zone;

at least one electrode secured to the wall of the second portion; and

a plurality of nozzles disposed at the bottom of the first portion for introducing fluidizing gas into the furnace.

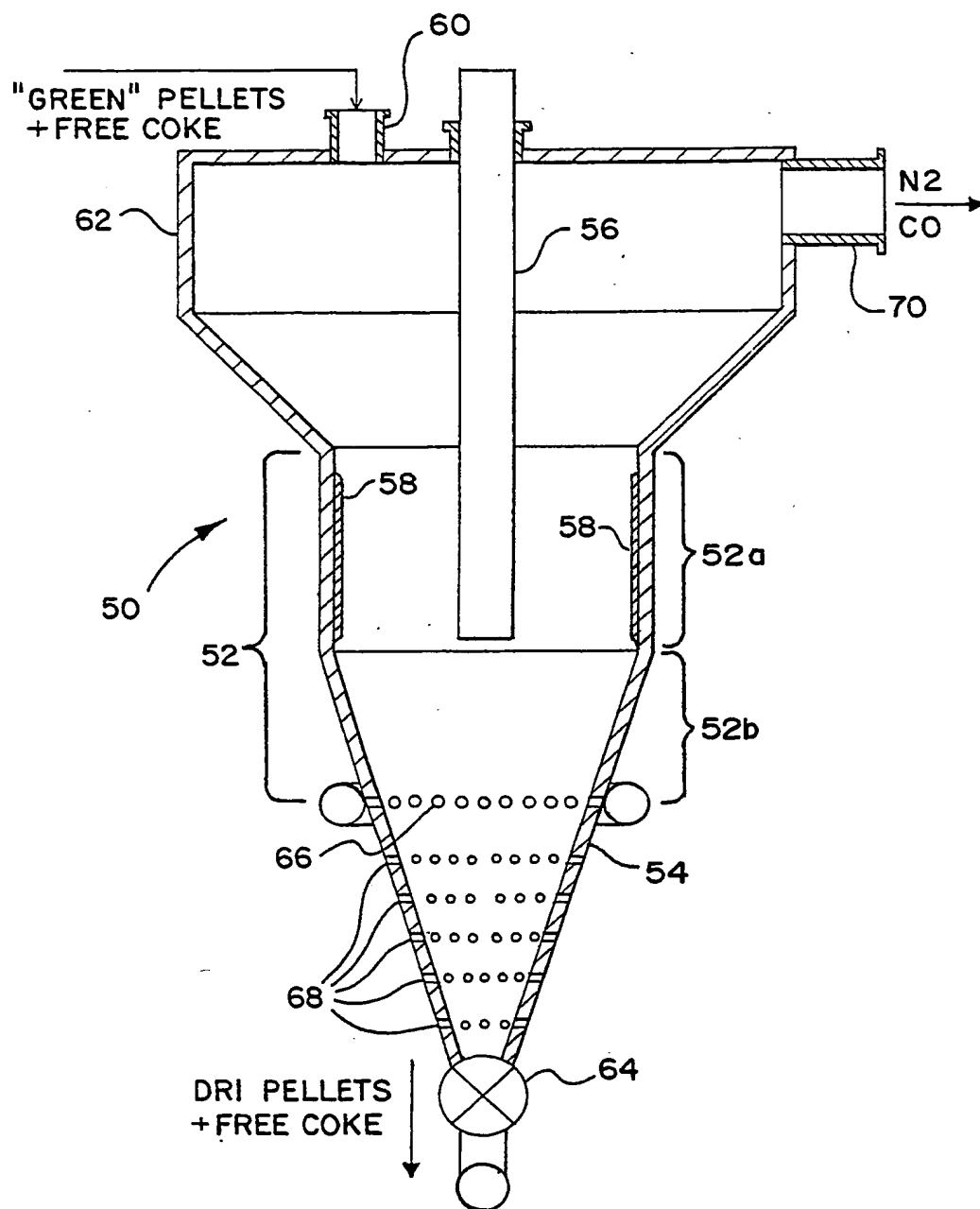
36. The electrothermal fluidized bed furnace of Claim 35 wherein the first section comprises a conical section defining a central angle of from  $30^{\circ}$  to  $90^{\circ}$ .

37. The electrothermal fluidized bed furnace of Claim 35 wherein the first section comprises a conical section defining a central angle of from  $40^{\circ}$  to  $60^{\circ}$ .

38. The electrothermal fluidized bed furnace of Claim 35 wherein the cross-sectional area of the second portion is from 1.5 to 2.5 times larger than the cross-sectional area of the first portion.

39. The electrothermal fluidized bed furnace of Claim 35 wherein the first and second portions have circular cross-sections and the diameter of the second portion is from 1.5 to 2.5 times larger than the diameter of the first portion.

FIG. 1



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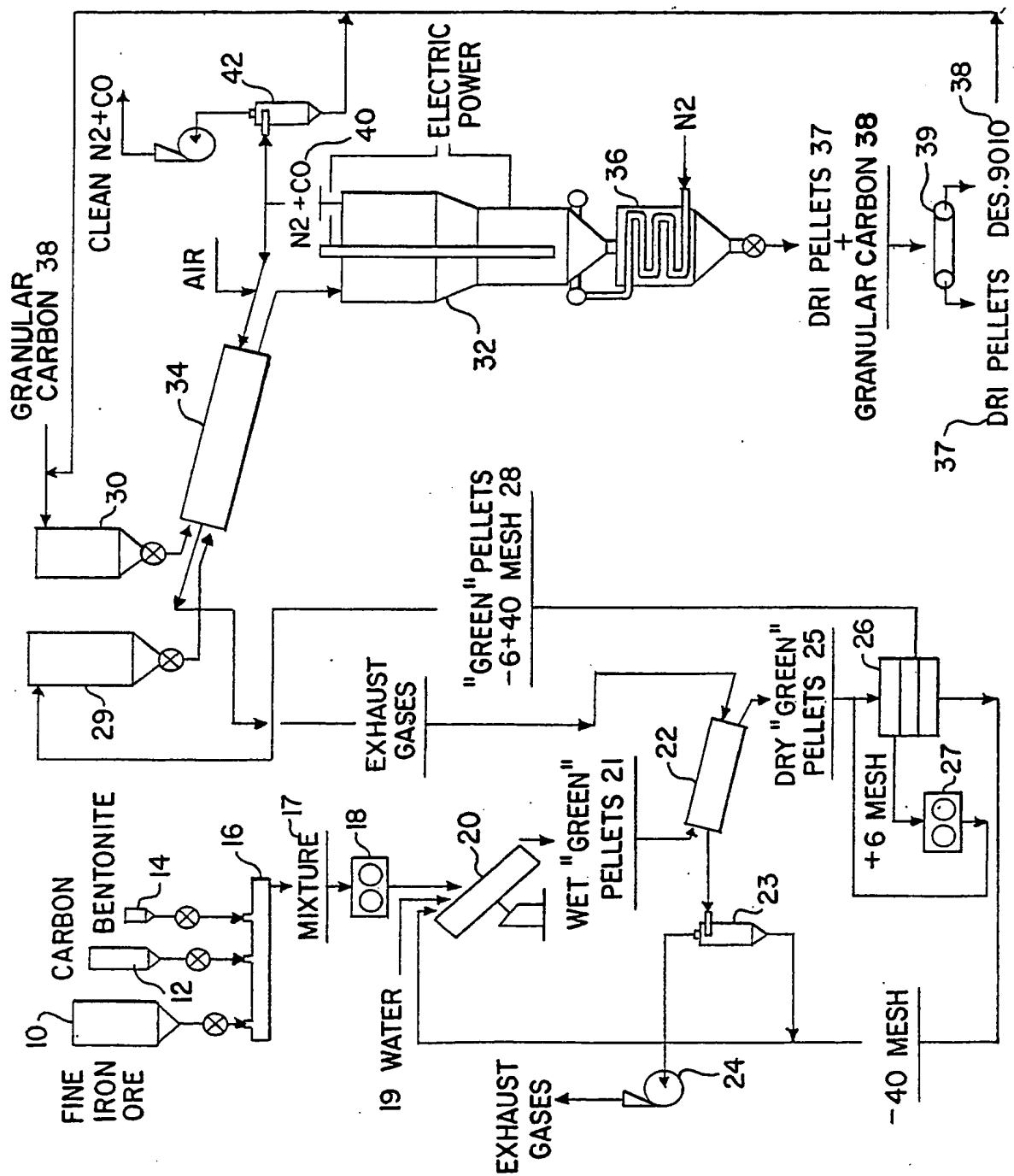


FIG. 2

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# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/08347

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : C21B 13/12; C22B 5/14, 23/00, 34/22, 34/32, 34/36; H05B 3/60

US CL : 75/10.1, 10.38, 10.63, 316; 266/172; 373/128

\*According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 75/10.1, 10.38, 10.63, 316; 266/172, 373/128

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)  
EAST: fluidized bed, iron, electrothermal, electrode

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 3,993,450 A (SCHORA JR et al.) 23 November 1976 (23.11.1976), column 1, lines 40-56	35-39
Y	US 4,178,170 A (IACOTTI et al) 11 December 1979 (11.12.1979), column 2, lines 30-60	17
Y	US 4,224,056 A (TOMIZAWA et al) 23 September 1980 (23.12.1980) column 12, line 55 to column 14, line 19	1-39
Y	US 6,071,468 A (MIYASHITA et al) 06 June 2000 (06.06.2000) column 20, line 19 to column 23, line 42	1-39

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

* Special categories of cited documents:	
"A" document defining the general state of the art which is not considered to be of particular relevance	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"Y" documents of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"O" document referring to an oral disclosure, use, exhibition or other means	"&" document member of the same patent family
"P" document published prior to the international filing date but later than the priority date claimed	

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25 July 2003 (25.07.2003)

Date of mailing of the international search report

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